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(54) Emulsifier based on an alkaline earth metal lanolate or other metal lanolate and water-in-oil emulsions based on this emulsifying system

(57) The present invention relates to an emulsifying system comprising an alkaline earth metal lanolate or other metal lanolate and a sterol, the said lanolate being obtained by the direct action of lanolin acid and an alkaline earth metal acetate or other metal acetate, in an anhydrous medium.

Water-in-oil emulsions containing this emulsifying system are useful as cosmetic and pharmaceutical emulsions.

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SPECIFICATION

Emulsifier based on an alkaline earth metal lanolate or other metal lanolate and water-in-oil emulsions based on this emulsifying system

The present invention relates to a new emulsifying system which takes the form of a mixture of an alkaline earth lanolate or metal lanolate and a sterol, and the use of this emulsifying system for the production of water-in-oil emulsions generally for the cosmetics or pharmaceuticals industry.

French Patent No. 72/10843, describes using as an emulsifying system for "water-in-oil" emulsions a mixture consisting of a lanolate chosen from magnesium, calcium, lithium, zinc and aluminium lanolates, together with hydrogenated lanolin and/or lanolin alcohol.

According to this patent, the emulsions obtained are described as being more economical since, inter alia, they are richer in water and possess good stability on storage at temperatures far removed from room temperature.

From the cosmetics standpoint, these emulsions do not, however, possess all the desirable properties generally sought for creams intended for application on the face. These water-in-oil emulsions in effect lack manageability, and have some tendency to whiten the skin on application.

Moreover, the use of hydrogenated lanolin and/or lanolin alcohol gives rise to certain difficulties, not only on account of the cost of these raw materials but also on account of the fluctuations in their quality, due to peroxidation leading to the formation of odours and to colour changes.

In order to confer greater manageability and to overcome the disadvantages of the emulsions of French Patent 72/10843, various co-emulsifiers of lanolates have been tested, in particular sterols such as cholesterol.

While the emulsions obtained were more manageable and more pleasant when applied, they nevertheless proved to be inferior in stability to those of French Patent No. 72/10843.

After many studies were conducted on this emulsifying system consisting of a lanolate and a sterol, it was established that the problem of the stability of the emulsions was linked to the nature of the co-emulsifier, that is to say the sterol, but to the lanolate itself according to the synthesis process used.

French Patent No. 72/10843 discloses preparing the lanolates by the following two methods:

1—Either by double decomposition, which method consists in first producing the sodium or potassium salt of lanolin acid in dilute form such that it is in homogenous solution, and then precipitating from this solution the desired lanolin acid salt, by adding a solution of an inorganic salt, for example a chloride,

2—or by direct action of an alkali metal hydroxide, alkaline earth hydroxide or metal hydroxide on lanolin acid.

Common to these two processes is the fact that they are performed in an aqueous medium and that this consequently results in the presence of some undesirable basic soaps which are difficult to remove.

Since the presence of these basic soaps is capable of impairing the stability of the emulsions when the lanolate is combined with a sterol, other processes for preparing lanolates were tried, in particular the process which consists in directly reacting lanolin acid with an alkaline earth acetate or metal acetate and removing the acetic acid formed, by heating under vacuum.

It was then observed, quite surprisingly, that lanolates prepared by the latter process, combined with a sterol such as cholesterol, led to very stable water-in-oil emulsions which possessed good spreading properties.

Moreover, the lanolates obtained by this process possess better solubility in the fatty phase of the emulsions as a result of the complete absence of basic soaps.

The present invention provides an emulsifier suitable for emulsifying water-in-oil emulsions, which comprises at least one alkaline earth metal lanolate or other metal lanolate and a sterol, the said lanolate being one obtained by the direct action of lanolin acid and an alkaline earth metal acetate or other metal acetate in an anhydrous medium.

According to the invention, the alkaline earth metal lanolates and metal lanolates are preferably calcium, magnesium, zinc, copper or aluminium lanolates.

The alkaline earth metal lanolates, in particular magnesium lanolate, make it possible to produce excellent water-in-oil emulsions having good stability and ease of application, due to the good spreading properties.

As stated above, the process for producing the lanolates which are intended for use in combination with a sterol as co-emulsifier is of fundamental importance.

This process, which is simple to carry out, consists in directly reacting, in an anhydrous medium, lanolin acid and an alkaline earth metal acetate or other metal acetate, and removing the acetic acid formed, by heating under vacuum, thereby enabling the equilibrium to be shifted

to the maximum.

The reaction is generally performed under nitrogen at a temperature from 80 to 150°C for a sufficient length of time to remove by distillation under vacuum the maximum amount of acetic acid formed during the reaction.

The yield of the reaction is generally from 90 to 99% relative to the starting lanolin acid.

If so desired, the lanolates obtained can subsquently be purified by adding to the mixture an aromatic solvent such as toluene, which enables any traces of acetic acid still present to be removed by azeotropic distillation at a temperature from 100 to 140°C.

According to a variant of this process, the reaction between lanolin acid and the alkaline earth metal acetate or metal acetate can be performed and completed in the presence of a cosmetically or pharmaceutically acceptable oil of high boiling point, such as, for example, liquid paraffin

At the end of the reaction, the lanolates are obtained in solution in an oil which can constitute a portion of the fatty phase of a water-in-oil emulsion.

Among the sterols which can be used as co-emulsifiers of the emulsifying system, very special mention may be made of cholesterol and β-sitosterol.

In the emulsifying system, the weight ratio of lanolate/sterol is from approximately 95:5 to 50:60, the preferred ratio being approximately 90:10.

According to a variant of the invention, the alkaline earth metal lanolate or other metal lanolate can be combined with at least one alkaline earth metal salt or other metal salt or another fatty acid, such as, for example, a stearate or oleate of calcium, magnesium, zinc, copper or aluminium, the proportion of the alkaline earth metal salt or metal salt of this other fatty acid generally not being greater than 25% by weight relative to the weight of the alkaline earth metal or other metal lanolate.

According to this variant, the mixture of alkaline earth metal lanolate or other metal lanolate and alkaline earth metal salt or other metal salt of another fatty acid is obtained using the process as described above, but starting with a mixture of lanolin acid and the other fatty acid which it is desired to combine in the chosen proportion.

The present invention also has as its subject manageable water-in-oil emulsions containing a water phase, a fatty phase and an emulsifying system as defined above.

These emulsions, which can comprise cosmetic or pharmaceutical vehicles, typically have a viscosity of from 80 to 85 poises, that is to say lower than those of the emulsions of French Patent No. 72/10843, which are of the order of 100 to 110 poises.

In these emulsions, the concentration of emulsifying system is generally from 3 to 20%, and preferably from 5 to 12%, relative to the total weight of the emulsion.

The ratio by weight of the fatty phase to the emulsifier is from 95:5 to 50:50, but this ratio is preferably approximately 90:10.

Among the fatty products forming the fatty phase of the emulsions, the following may be mentioned:

—hydrocarbon oils such as liquid paraffin, purcellin oil, perhydrosqualene, and solutions of microcrystalline waxes in the oils,

—animal or vegetable oils, such as sweet almond oil, avocado oil, oil of calophyllum, lanolin, castor oil, horse oil, pig oil, sesame oil, olive oil, jojoba oil, shea-nut oil, oil of hoplostethus,

—mineral oils, the initial distillation point of which at atmospheric pressure is approximately 250°C and the final point of the order of 410°C,

—saturated or unsaturated esters, such as alkyl myristates, for example isopropyl, butyl or cetyl myristates, hexadecyl stearate, ethyl or isopropyl palmitates, triglycerides of octanoic or decanoic acids or cetyl ricinoleate.

The fatty phase can also contain silicone oils soluble in the other oils, such as dimethylpolysiloxane, methylphenylpolysiloxane and silicone/glycol copolymer.

In order to promote retention of the oils, waxes can also be used such as carnauba wax, candelilla wax, beeswax, microcrystalline wax or ozokerite.

When the emulsions are intended for cosmetic use, they can take the form of e.g. moisturising suntan creams or moisturising creams for the face, body or hands, as well as the form of moisturising blushers or of making foundations. In this case, concentration of the water phase of the emulsion is generally from 20 to 70%, but preferably from 40 to 60%, by weight relative to the total weight of the emulsion.

These compositions can also take the form of moisturising suntan sticks or moisturising sticks for the face or body, as well as the form of lipsticks or eye makeup sticks. In this case, the concentrations of the water phase in the emulsion is generally from 5 to 70% by weight relative to the total weight of the emulsion.

The cosmetic compositions can contain all the ingredients generally used in cosmetics, and especially colourings, pigments, sunscreens, perfumes, preservatives such as methyl para-hydroxybenzoate or propyl para-hydroxybenzoate, as well as co-emulsifiers such as, for example, the product sold by Goldschmidt under the name "PROTEGIN W".

These compositions can, in addition, contain certain active principles, not only for the maintenance of the skin but also to improve its properties, in particular its elasticity.

Among these substances, special mention may be made of humectants such as thiamorpholinone and its derivatives, vitamins, revitalising agents, protein derivatives such as elastin and collagen, and the like.

The emulsions can also constitute a vehicle for certain therapeutic active principles, the compositions taking the form of creams.

Among the active substances preferred for this type of vehicle, special mention may be made of the following:

—anti-inflammatory agents, especially corticoids such as hydrocortisone, difluprednate, β-methasone or dexamethasone,

—antibiotics such as erythromycin, clindamycin or neomycin,

—keratolytics such as retinoic acid or benzoyl peroxide,

—antipsoriasic agents, such as anthralin and its derivatives and etretinate,

—vitamins and derivatives such as vitamin A palmitate, biotin or d-panthenol,

—antifungals, such as imidazole derivatives or tolnaftate, and

—natural or synthetic sex hormones, such as progesterone or testosterone.

The process for preparing the water-in-oil emulsions typically consists, in a first stage, in dissolving the lanolate in the fatty phase at a temperature of approximately 100°C and with strong agitation, and in the second stage, adding the sterol at a temperature of approximately 80°C, after which the mixture is cooled to a temperature of approximately 40°C and the water phase, brought beforehand to the same temperature, is introduced with strong agitation, and the emulsion is then cooled to room temperature while stirring. If so desired, the emulsion can be refined by passing it through a roller crusher.

This process as has just been described above more especially enables creams to be obtained. For the production of sticks, the water is heated beforehand to 80°C and added to the uncooled mixture, and the emulsion obtained is then poured at this temperature into suitable moulds for the formation of sticks.

The following Examples further illustrate the preparation of various alkaline earth metal lanolates and other metal lanolate, as well as several "water-in-oil" emulsions for cosmetic or pharmaceutical use.

PREPARATION OF LANOLATES

Preparation of zinc lanolate

221.7 g of lanolin acid (0.5 mol) is placed in a suitable vessel equipped with a device for removing acetic acid under vacuum by distillation, and with a nitrogen inlet.

The vessel is heated to a temperature of 80°C until the lanolin acid melts, and 53.77 g of zinc acetate $2H_2O$ (0.245 mol) are then added in a single portion.

The mixture is then brought to 120–125°C for the purpose of removing by distillation the water and acetic acid formed. A vacuum is then gradually applied to the installation (1.99 Kpa) and the temperature is gradually brought to 137°C.

After 35 min, a first distillate of acetic acid and water (37 g) is obtained, followed by a second distillate (1.66 g) after 40 min at a temperature of approximately 130–135°C under 1.99 Kpa.

100 g of toluene are then added, and azeotropic distillation of the remaining traces of acetic acid is then performed at atmospheric pressure and at a temperature of 120 to 130°C.

The latter treatment enables the acetic acid to be removed to the extent of 97.6% relative to the theoretical extent.

Zinc lanolate (233.6 g) is obtained in a 98% yield, and has a total acidity of 2.075 meq/g (theory: 2.11 meq/g).

Preparation of copper lanolate

In a suitable vessel equipped with a device for removing acetic acid under vacuum by distillation and with a nitrogen inlet, 221.7 g of lanolin acid (0.5 mol) are introduced and brought to 90°C under nitrogen until complete melting has occurred.

50 g (0.245 mol) of copper acetate monohydrate are then added and the mixture is brought with stirring to a temperature between 117 and 125°C. After the distillation has slowed down, the installation is placed under vacuum and the temperature gradually increased to 135°C under 1.99 Kpa.

A first distillate (33.7 g) of acetic acid and water is thus obtained, followed by a second distillate (1.15 g) after one hour under 1.99 Kpa at 135°C.

Subsequent purification did not prove to be necessary, since the copper lanolate obtained no longer has residual traces of acetic acid. 252 g of copper lanolate are thus obtained in a yield of 100%.

Preparation of magnesium lanolate

In a 6-litre three-necked flask equipped with a device for distillation under vacuum and a nitrogen inlet, 2,444.2 g of lanolin acid (5.5 mol) are introduced and brought to approximately 90°C under nitrogen. After the lanolin acid has melted, 578.2 g of magnesium acetate $4H_2O$ (2.7 mol) are then added in a single portion and heating is continued to approximately 108°C. At this temperature, the acetic acid and water or hydration of the magnesium acetate begin to distill. The temperature of the reaction mixture is then brought gradually to 130°C while distilling off the acetic acid formed.

The temperature is maintained at 130°C for approximately 2 hours and then, when the distillation has slowed down, the installation is placed under vacuum in order to promote the removal of the remaining acetic acid.

After 1 hour at 130–135°C under 1.99 Kpa, a first distillate (461 g) is obtained, 2,505 g of liquid paraffin are then added and heating is continued at 130–135°C under vacuum (6.65 Pa) for 1 hour and a second distillate (47 g) is obtained.

The magnesium lanolate in 50% strength solution in liquid paraffin can be used as it is to produce water-in-oil emulsions.

COSMETIC COMPOSITIONS

EXAMPLE 1: Lipstick

Calcium lanolate, 50% strength in liquid paraffin	17.00 g
Cholesterol	3.00 g
Beeswax	3.00 g

Castor oil ..... 10.00 g

Liquid paraffin ..... 12.00 g

Colourings D and C orange No. 17 ..... 0.50 g

Colourings D and C red 8 ..... 0.50 g

Titanium oxide ..... 2.30 g

Water + 0.2% methyl para-hydroxybenzoate ...QS 100.00 g

EXAMPLE 2: Moisturising stick for the body

Magnesium lanolate, 50% strength in liquid paraffin ..... 8.10 g

Cholesterol ..... 0.90 g

Purcellin oil ..... 3.00 g

Liquid paraffin ..... 12.00 g

Ozokerite ..... 8.00 g

Water + 0.2% methyl para-hydroxybenzoate .. QS 100.00 g

EXAMPLE 3: Moisturising stick for the face

Magnesium lanolate, 50% strength in liquid paraffin ..... 12.00 g

Cholesterol ..... 8.00 g

Perhydrosqualene ..... 5.00 g

Ozokerite ..... 15.00 g

Water + 0.2% methyl para-hydroxybenzoate .. QS 100.00 g

EXAMPLE 4 - Moisturising treatment cream

Copper lanolate ..... 3.32 g

Cholesterol ..... 0.35 g

Liquid paraffin ..... 23.33 g

Sunflower oil ..... 10.00 g

Lanolin ..... 5.00 g

Water + 0.2% methyl para-hydroxybenzoate .. QS 100.00 g

EXAMPLE 5 - Moisturising makeup foundation

Zinc lanolate ..... 6.37 g

Cholesterol ..... 2.25 g

Vaseline ..... 10.00 g

Liquid paraffin ..... 26.38 g

Iron oxide + titanium oxide ..... 7.00 g

Water + 0.2% methyl para-hydroxybenzoate .. QS 100.00 g

EXAMPLE 6 - Moisturising suntan cream

Calcium lanolate, 50% strength in liquid paraffin ..... 6.65 g

Cholesterol ..... 0.35 g

Liquid paraffin ..... 20.00 g

Silicone oil ..... 10.00 g

Sunscreen "PARSOL 1789" (butylmethoxydibenzoyl-methane) sold by GIVAUDAN ..... 3.00 g

Water + 0.2% methyl para-hydroxybenzoate .. QS 100.00 g

EXAMPLE 7 - Tinted moisturising cream

Magnesium lanolate, 50% strength in liquid paraffin ..... 6.00 g

β-Sitosterol ..... 4.00 g

Liquid paraffin ..... 29.00 g

Silicone oil ..... 3.00 g

Purcellin oil ..... 5.00 g

Iron oxide + titanium oxide ..... 3.00 g

Water + 0.2% methyl para-hydroxybenzoate .. QS 100.00 g

EXAMPLE 8 - Moisturising after-suntan cream

Magnesium lanolate, 50% strength in liquid paraffin	17.00 g
Cholesterol	3.00 g
Isopropyl myristate	10.00 g
Liquid paraffin	38.00 g
Beeswax	5.00 g
Lanolin	5.00 g
D-Panthenol	2.00 g
Water + 0.2% methyl para-hydroxybenzoate	QS 100.00 g

EXAMPLE 9 - Moisturising cream for the face

Magnesium lanolate, 50% strength in liquid paraffin	5.70 g
Cholesterol	0.15 g
Liquid paraffin	23.15 g
Isopropyl palmitate	4.00 g
Purcellin oil	3.00 g
Sesame oil	4.00 g
Water + 0.2% methyl para-hydroxybenzoate	QS 100.00 g

EXAMPLE 10: Moisturising skin care cream

Magnesium lanolate, 50% strength in liquid paraffin	2.85 g
Cholesterol	0.15 g
Liquid paraffin	4.00 g
Protegin W sold by Goldschmidt	30.00 g
Water + 0.2% methyl para-hydroxybenzoate	QS 100.00 g

CLAIMS

1. An emulsifier suitable for emulsifying water-in-oil emulsions, which comprises at least one alkaline earth metal lanolate or other metal lanolate and a sterol, the said lanolate being one obtained by the direct action of lanolin acid and an alkaline earth metal acetate or other metal acetate in an anhydrous medium.

2. An emulsifier according to Claim 1, in which the alkaline earth lanolate or metal lanolate is a calcium, magnesium, zinc, copper or aluminium lanolate.

3. An emulsifier according to Claim 1 or 2 in which the sterol is cholesterol of β-sitosterol.

4. An emulsifier according to any one of the preceding claims, in which the weight ratio of lanolate/sterol is from 95:5 to 40:60.

5. An emulsifier according to Claim 4 in which the weight ratio is approximately 90:10.

6. An emulsifer according to Claim 1 in which the lanolate is produced substantially according to any one of the preparation examples described herein.

7. A water-in-oil emulsion containing a water phase, a fatty phase and an emulsifier as claimed in any one of Claims 1 to 6.

8. An emulsion according to Claim 7, which has a viscosity of from 80 to 85 poises.

9. An emulsion according to Claim 7 or 8 in which the concentration of emulsifier is from 3 to 20% by weight relative to the total weight of the emulsion.

10. An emulsion as claimed in Claim 9 in which the concentration is from 5 to 12% by weight.

11. An emulsion according to any one of Claims 7 to 10, in which the weight ratio of the fatty phase to the emulsifier is from 95:5 to 50:50.

12. An emulsion as claimed in Claim 11 in which the weight ratio is approximatelt 90:10.

13. An emulsion according to any one of Claims 7 to 12, which is in the form of a cream and contains the water phase at a concentration of from 20 to 70% by weight relative to the total weight of the emulsion.

14. An emulsion according to Claim 13 in which the water phase concentration is from 40 to 60%.

15. An emulsion according to any one of Claims 7 to 12, which is in the form of a stick and contains the water phase at a concentration of from 5 to 70% by weight relative to the total weight of the emulsion.

16. An emulsion according to any one of Claims 7 to 15, which contains at least one active ingredient having a cosmetic or therapeutic action, as well as any conventional ingredient of cosmetic or therapeutic compositions.

17. An emulsion as claimed in Claim 7 substantially as described in any one of Examples 1 to 10.

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